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Smart Structures and Materials 1996: Smart Materials Technologies

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Abstracts:

Paper #: 2716-01
Smart materials based on polymeric systems, pp.2-7
Author(s): Andrew Crowson, U.S. Army Research Office, Research Trian Park, NC, USA.

Abstract: The science and technology of the 21st century will rely heavily on the development of new materials. Such materials are expected to be innovative with regards to structure, functionality, and design. One concept in achieving this goal is what has been termed 'smart materials.' A smart material is defined as a material which has been atomically or molecularly engineered in such a way that the microstructure itself is imbued with embedded sensors, actuators, and control mechanisms, giving it the capability of sensing and responding to external stimuli in a predetermined and controlled fashion. Programs in this area have involved technological advances in a number of scientific disciplines inclusive of materials science, chemistry, biotechnology, molecular electronics, nanotechnology, etc. These have encompassed research themes into the design of polymeric materials which are capable of altering their mechanical and electrical properties when exposed to specific molecular species, the synthesis of amphiphlic molecules with easily modified ferroelectric, photochromic and nonlinear properties, the design of stress sensitive molecules capable of monitoring damage and redistributing stresses in composites, and the merging of biological and chemical technologies to create assemblies with signal transduction properties. This presentation highlights some of these activities. !15

Paper #: 2716-02
Assembly of conducting polymer networks inside hydrogel structures, pp.8-19
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Abstract: The development of novel conducting polymer hydrogel composites has been pursued in the course of this work. It has been found that conducting polymers can be formed electrochemically within hydrogel structures. This enables the dimensions and shape of conducting polymer based structures to be easily modified. The resulting composites retain the properties of the hydrogels and also are electroactive. Preliminary work suggests that these structures show enhanced performance when used as electromolecular or electromechanical actuators. !11

Paper #: 2716-04
Smart materials for polymer-stabilized reflective cholesteric displays, pp.20-27
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Abstract: Liquid crystal/polymer network composites are formed by mixing small amounts of mesogenic monomers and liquid crystals. The monomers are then photo-polymerized in liquid crystalline phases. The polymer networks, whose orientation is controlled by the surface alignment or external field, are anisotropic. Afterwards, we use the resultant ordered networks, influenced by the orientation of liquid crystals, to stabilize cholesteric textures and develop three different types of displays. A tunable chiral material (TCM), whose chirality can be photochemically altered by exposing the materials to UV light, is integrated into the production of a multicolor reflective cholesteric display. !25

Paper #: 2716-05
Plastic retina: image enhancement using polymer grid triode arrays, pp.28-35
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Abstract: An array of polymer grid triodes (PGTs) connected through a common grid functions as a 'plastic retina' which provides local contrast gain control for image

enhancement. This device, made from layers of conducting polymers, functions as an active resistive network that performs center-surround filtering. The PGT array with common grid is a continuous analog of the discrete approach of Mead, with a variety of fabrication advantages and with a significant saving of 'real estate' within the unit cell of each pixel. !10

Paper #: 2716-07
Electrically controllable ionic polymeric gels as adaptive optical lenses, pp.36-45
Author(s): Karim Salehpoor, Univ. of New Mexico, Albuquerque, NM, USA;
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Abstract: Reversible change in optical properties of ionic polymeric gels, 2-acrylamido-2-methylpropane sulfonic acid (PAMPS) and polyacrylic acid plus sodium acrylate cross-linked with bisacrylamide (PAAM), under the effect of an electric field is reported. The shape of a cylindrical piece of the gel, with flat top and bottom surfaces, changed when affected by an electric field. The top surface became curved and the sense of the curvature (whether concave or convex) depended on the polarity of the applied electric field. The curvature of the surface changed from concave to convex and vice versa by changing the polarity of the electric field. By the use of an optical apparatus, focusing capability of the curved surface was verified and the focal length of the deformed gel was measured. The effect of the intensity of the applied electric field on the surface curvature and thus, on the focal length of the gel are tested. Different mechanisms are discussed; either of them or their combination may explain the surface deformation and curvature. Practical difficulties in the test procedure and the future potential of the electrically adaptive and active optical lenses are also discussed. These adaptive lenses may be considered as smart adaptive lenses for contact lens or other optical applications requiring focal point undulation. !33

Paper #: 2716-08
Thermomechanical properties in a thin film of shape memory polymer of polyurethane series, pp.46-57
Author(s): Hisaaki Tobushi, Aichi Institute of Technology, Toyota, Japan;
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Abstract: The thermomechanical properties of a thin film of shape memory polymer of polyurethane series were investigated experimentally. The results were summarized as follows: (1) Modulus of elasticity and yield stress are high below glass transition temperature T$-g$/ and low above T$-g$/. The value of loss tangent is large in the vicinity of T$-g$/. (2) The stress-strain curves vary significantly in the early cycles but slightly thereafter under cyclic deformation above T$- g$/. (3) During the heating process after loading above T$-g$/ followed by unloading below T$-g$/, strain is recovered in the vicinity of T$-g$/. (4) Shape fixity with loading above T$- g$/ followed by unloading below T$-g$/ does not vary under thermomechanical cycling. (5) Creep strain is recovered after unloading above T$-g$/. Creep residual strain below T$-g$/ is recovered in the vicinity of T$-g$/ during the heating process. (6) About a half of initial stress relaxes after a certain duration of time. Several applications of the polymers were introduced. !7

Paper #: 2716-11
Determination of the voltage-dependent dielectric properties of piezoelectric materials with a high-voltage/high-power electromechanical impedance analyzer, pp.60-68
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Abstract: The dielectric properties of piezoelectric materials are important in many applications of piezoelectric materials, such as active structural control, underwater sonar, dielectric insulator, etc. The experimental measurement of dielectric properties of materials is usually done using commercial electrical impedance analyzer, LCR meter, or network analyzer, such as an HP 4194 impedance analyzer. The excitation voltage of these commercial analyzers is generally very low, e.g., 1.5 volts rms or under. However, the dielectric properties of piezoelectric materials (both dielectric constant and dielectric loss factor) can be very sensitive to the level of applied electric voltage (field). Since virtually all the applications of piezoelectric materials are under high field, it is important to develop measurement techniques to determine the voltage dependent dielectric material properties. This paper introduces a high-voltage/high-power electromechanical impedance analyzer developed based on a commercial electrical power analyzer/phase angle multimeter. The developed analyzer is then used to determine the dielectric constant and dielectric loss factor of G1195 PZT. The measurement results, dielectric constant and loss factor as a function of applied electric field, frequency, and

ambient temperatures, are presented in the paper. !5

Paper #: 2716-12
Sol-gel-derived PZT fibers: development and limitations, pp.69-79
Author(s): Richard Meyer, Jr., The Pennsylvania State Univ., University Park, PA, USA;
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Abstract: Fine scale lead zirconate titanate (PZT) fibers were fabricated from sol-gel processed viscous 'sol' using spinning methodology developed for the continuous production of glass and carbon fibers. Subsequent drying and firing at temperatures above 700 degrees Celsius resulted in phase pure perovskite fibers with diameters ranging from 30 to 70 micrometers. The dense fibers were comprised of sub-micron grains at sintering temperatures below 1000 degrees Celsius, growing to 2 - 3 micrometers at 1200 degrees Celsius. The dielectric properties of the sol-gel derived fibers were comparable with that of bulk ceramics for both undoped and modified PZT compositions. Relevant to mechanical properties, however, the fine scale PZT fibers exhibited fracture strengths on the order of 50 MPa, well below that of structural fiber materials, e.g. Al-2/O-3/, limiting their potential use in active structural composites. !6

Paper #: 2716-13
Optomechanical actuator in the form of graphite, pp.80-84
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Abstract: Optomechanical actuation was achieved reversibly using highly oriented pyrolytic graphite intercalated with bromine (1.9 mol% Br-2/). White light from a 150 W tungsten-halogen lamp was used for optomechanical switching. The displacement was approximately 4 micrometers and occurred only along the c-axis of the graphite. The rise and fall times were approximately 15 s. The origin of the optomechanical effect is the reversible exfoliation of the near surface region of the intercalated graphite. !3

Paper #: 2716-15
Response of a two degree of freedom system incorporating an electrorheological damper, pp.85-94
Author(s): Janusz Goldasz, Univ. of Strathclyde, Glasgow, United Kingdom;
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Abstract: Electrorheological (ER) fluids are fine semi-conducting

particles in a non-conducting carrier fluid, which can alter their observed physical characteristics upon application of an external electric field. They are sometimes referred to as 'smart materials' and would appear to be of scientific and industrial interest. Theoretical responSe of a two degree of freedom system utilizing an ER damper is shown. This model could be representative of a quarter vehicle system, or a vibration absorber. !15

Paper #: 2716-16
Shape memory characteristics of Ti-Ni alloys with several specimen sizes from micrometer to millimeter, pp.95-103
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Abstract: Ti-Ni shape memory alloys with nearly equiatomic compositions were made by three types of production methods, i.e., rolling, drawing and sputtering methods. These methods were used for making thin plates 0.1 mm thick, thick and thin wires 1.0 mm and 0.08 mm in diameter, and thin films 0.007 mm thick, respectively. These specimens were annealed at 673 K, 773 K, and 873 K in order to investigate the affect of annealing temperature on the shape memory characteristics in each specimen. The shape memory characteristics were compared among these specimens in order to investigate the effect of the production method. !21

Paper #: 2716-17
Thermomechanical properties due to martensitic and R-phase transformations of Ti-Ni shape memory alloy subjected to cyclic loadings, pp.104-115
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Abstract: The thermomechanical properties of shape memory effect and superelasticity due to the martensitic transformation and the R-phase transformation of TiNi shape memory alloy were investigated experimentally.

The transformation line, recovery stress and fatigue property due to both transformations were discussed for cyclic deformation. The thermomechanical properties due to the R-phase transformation were excellent for deformation with high cycles. !21

Paper #: 2716-18
Electrically controllable artificial PAN muscles, pp.116-124
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Abstract: Artificial muscles made with polyacrylonitrile (PAN) fibers are traditionally activated in electrolytic solution by changing the pH of the solution by the addition of acids and/or bases. This usually consumes a considerable amount of weak acids or bases. Furthermore, the synthetic muscle (PAN) itself has to be impregnated with an acid or a base and must have an appropriate enclosure or provision for waste collection after actuation. This work introduces a method by which the PAN muscle may be elongated or contracted in an electric field. We believe this is the first time that this has been achieved with PAN fibers as artificial muscles. In this new development the PAN muscle is first put in close contact with one of the two platinum wires (electrodes) immersed in an aqueous solution of sodium chloride. Applying an electric voltage between the two wires changes the local acidity of the solution in the regions close to the platinum wires. This is because of the ionization of sodium chloride molecules and the accumulation of Na$+$PLU$/ and Cl$+MIN/ ions at the negative and positive electrode sites, respectively. This ion accumulation, in turn, is accompanied by a sharp increase and decrease of the local acidity in regions close to either of the platinum wires, respectively. An artificial muscle, in close contact with the platinum wire, because of the change in the local acidity will contract or expand depending on the polarity of the electric field. This scheme allows the experimenter to use a fixed flexible container of an electrolytic solution whose local pH can be modulated by an imposed electric field while the produced ions are basically trapped to stay in the neighborhood of a given electrode. This method of artificial muscle activation has several advantages. First, the need to use a large quantity of acidic or alkaline solutions is eliminated. Second, the use of a compact PAN muscular system is facilitated for applications in active musculoskeletal structures. Third, the PAN muscles become electrically controllable and therefore the use of such artificial muscles in robotic structures and applications becomes more feasible. A muscle is designed such that it is exposed to either Na$+$PLU$/ or Cl$+MIN/ ions effectively.

Muscle contraction or expansion characteristics under the effect of the applied electric field are discussed. !33

Paper #: 2716-20
Design of environment-responsive biomolecular systems, pp.126-132
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Abstract: Two different types of biomolecular network systems have been designed to respond to the environmental conditions. One is the calmodulin and enzyme (phosphodiesterase, PDE) that activates phosphodiesterase through the conformational change in responding calcium ion. Calmodulin was genetically engineered to be fused with glutathione-S-transferase (GST). Calmodulin/GST fused protein was self-assembled on the gold surface through glutathione. The calmodulin/GST protein layer exhibited an ability to modulate the PDE activity in a solution phase depending on the calcium ion concentration. The other is the engineered gene structure that produces firefly luciferase in responding environmental pollutants. A TOL plasmid, encoding a binding protein xyl R for xyline and a marker enzyme firefly luciferase, has been implemented in a bacterial cell. The whole cell responded to environmentally hazardous substances such as xylene in emitting light. !3

Paper #: 2716-21
Space-resolved manipulation of biological macromolecules, pp.133-143
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Abstract: In conventional biochemistry, there has been no method to allow space-resolved access to a particular position in a molecule. This is due partly to a lack of the molecular manipulation method. A chain like macromolecule, such as DNA, takes randomly coiled conformation and fluctuates due to Brownian motion. Hence, to allow external access, it has to be immobilized with a proper conformation first. The authors use high-intensity high-frequency electric field (less than or equal to 10$+6$/ V/m, $APEQ 1 MHz) created in micro-machined electrodes to (1) stretch a flexible molecule, (2) align parallel to the field,

and/or (3) position onto a substrate either electrically or with the use of molecular bindings. It has been shown that DNA is stretched to full length (0.34 nm per base) under the electrostatic field. Once stretch-and- positioned, position-dependent modifications become possible. It is demonstrated that (1) a stretched DNA can be cut at arbitrary position by ultra-violet laser beam, (2) local temperature rise created by a laser manipulated-and-heated microbead induces pin-point conformational change of a bacterial flagellum ('tail'). The spatial resolution enabled by the electrostatic stretch-and-positioning will find applications not only in biochemical assays, in particular DNA sequencing, but also in the basic research of biomolecular interactions. !15

Paper #: 2716-22
Self-assembled and supported BLMs as an adaptive material for biotechnology, pp.144-151
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Abstract: Cell membranes play a vital role in energy conversion, information processing and signal transduction. This is owing to the fact that most physiological activities involve lipid bilayer- based receptor-ligand interactions. Some of the outstanding examples are ATP synthesis, ion transport, antigen-antibody binding, and gated channels. One approach to study these interactions in vitro is facilitated by employing artificial BLMs (bilayer lipid membranes). Our current efforts have been focused on ion and/or molecular selectivity and specificity using recently available self-assembled BLMs on solid support (i.e. s-BLMs) which, with their enhanced stability, greatly aid in research areas of membrane biochemistry, biophysics, and cell biology as well as in biosensor designs and molecular devices development. In this report, our recent work along with the experiments done in collaboration with others on s-BLMs are presented. !29

Paper #: 2716-24
Novel immobilization techniques in the fabrication of efficient electrochemical biosensors, pp.152-163

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Abstract: The development of enzyme electrodes plays a major role in the performance of an electrochemical biosensor. In this paper, we describe two generic methods for efficient immobilization of enzymes or biomolecules at the electrode surface. These methods are based on physical entrapment of the enzymes during biochemical polymerization of phenols and electrochemical copolymerization of aromatic diamines with enzymes that are covalently coupled to the monomer. Both of these techniques have proven to be chemically mild and provide efficient polymer matrices for the fabrication of enzyme electrodes. Enzymes including horseradish peroxidase, alkaline phosphatase and glucose oxidase have been immobilized in these polymeric matrices and used for electrochemical as well as colorimetric detection of various substrates. Response times of the order of 5 - 10 seconds and sensitivities of the order of mM have been achieved with these electrodes. The use of these immobilization techniques towards the development of microelectrode arrays for multianalyte sensors is also discussed. !19

Paper #: 2716-25
Integration of biocomponents with synthetic structures: use of conducting polymer polyelectrolyte composites, pp.164-176
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Abstract: New biocomposites with dynamically active properties were synthesized containing the conducting electroactive polymer, polypyrrole, dextran sulphate and a range of proteins. These composites have a hydrophilic matrix with a high water content and confer on the conducting polymer several properties useful in the design of new 'smarter' biomaterials. The composite is an excellent surface for the culture of mammalian cells. Inclusion of the polyelectrolyte also allows incorporation of protein and control of its release by reducing the polypyrrole backbone. These properties were exploited to incorporate nerve growth factor into a composite of polypyrrole and sulphated polysaccharide and after reduction to cause release of the nerve growth factor and thereby stimulate phaeochromocytoma cells to differentiate. Inclusion of polyelectrolyte also allows the incorporation of whole relatively intact cells into a polymer composite. This was demonstrated by the incorporation of human erythrocytes into the composite. The electrochemical properties of the composite were maintained raising the possibility that they could be used as the basis of an electrochemical biosensor for the detection of blood cell antigens. These new composite polymers showing protein release could be used not only as vehicles to deliver proteinaceous pharmaceuticals but also to communicate with mammalian cells during critical phases of their growth and development. The immobilization of mammalian cells in the composites could not only form the basis of biosensors but can also be used for many other applications where immobilized cells are required. Moreover the ability to control the dynamic properties of the composite and possibly the cells within it could be exploited to advantage. !33

Paper #: 2716-26
Nanospace interface for the electrochemical communication between redox-active biomolecules and metal oxide electrodes, pp.177-182
Author(s): Hiroaki Shinohara, Okayama Univ., Okayama, Japan.

Abstract: Oriented assembly and interfacial electron transfer of flavin coenzymes on titanium dioxide (TiO-2/) electrodes have been studied to develop the smart enzyme sensors or reactors. It was demonstrated that FMN and FAD were chemically adsorbed via phosphate moiety on TiO-2/ surface in weak acidic solutions to make monolayers. Quasi reversible slow electron

transfer was observed on the FMN or FAD-adsorbed TiO-2/ electrodes. It was further demonstrated that the FMN-assembled TiO-2/ electrode electrochemically catalyzed the oxidation of NADH. The FMN-assembled TiO-2/ was then combined with some dehydrogenases and NADH to perform amperometric sensing for enzyme substrates. The results suggest that the assembled flavin coenzyme might be promising for a nanospace interface to achieve electrochemical communication between redox active biomolecules and the metal oxide electrodes. !2

Paper #: 2716-27
Noiseless propulsion for swimming robotic structures using polyelectrolyte ion-exchange membrane, pp.183-192
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Abstract: In this paper a Nafion$+TM$/ polyelectrolyte ion-exchange membrane (IEM) was used as a propulsion fin for robotic swimming structures such as a boat or fish-like object swimming in water or aqueous medium. The Nafion membrane was chemically plated with platinum. The resulting membrane was cut in a strip to resemble a fish-like caudal fin for propulsion. A small function generator circuit was designed and built to produce approximately plus or minus 2.0 V amplitude square wave at varying frequency up to 50 Hz. The circuit board was mounted on a buoyant styrofoam shaped like a boat or a tadpole. The fin was attached to the rear of the boat. By setting the signal frequency to the desired value and thereby setting the frequency of bending oscillation of the membrane, a proportional forward propulsion speed could be obtained. The speed was then measured using a high speed camera. Several theoretical hydrodynamic models were then presented to characterize speed-frequency of the forward motion using available theories on biological fish motion. The results were compared to experimental data which showed close agreement. It turned out that the forward speed of the object was directly proportional to the product of frequency and amplitude of the fin oscillation as in biological fishes. This relation was further simplified by keeping the voltage constant and therefore amplitude of the oscillation. The proportionality constant could be measured for a known geometry of the fin-boat assembly and reactivity of the Nafion membrane used. The system as a whole presented an autonomous robotic swimming structure with frequency modulated propulsion to investigate application of polyelectrolyte hydrogel membranes and their effect on hydrodynamic behavior of an undulating swimming object. As in fishes the thrust force of the robot was generated by evolution of vortices on the sides of the undulating fin. For a constant forward speed, this thrust is equal to the drag force due to geometry and skin friction of the